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Conformationally rigid diphosphine arene–ruthenium(II) complexes as catalysts for transfer hydrogenation of ketones

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Abstract

Conformationally rigid [(η^6-arene)Ru(P–P)Cl]CF_3SO_3 (arene = C_6H_6 (**1**), *p*-$MeC_6H_5CHMe_2$ (**2**), 1,3,5-$Me_3C_6H_3$ (**3**), and Me_6C_6 (**4**); P–P is 2-diphenylphosphino-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene) compounds have been synthesized from [(η^6-arene)$RuCl_2$(DMPP)] (DMPP = 3,4-dimethyl-1-phenylphosphole) and diphenylvinylphosphine (DPVP) in the presence of $AgCF_3SO_3$. The structures of **2**, **3** and **4** were determined by X-ray crystallography. These complexes have been found to be quite effective catalysts for the transfer hydrogenation of ketones in 2-propanol in the presence of KOH.

Keywords: Phosphole; Vinylphosphine; [4+2]Diels–Alder cycloaddition; Ruthenium; Transfer hydrogenation

1. Introduction

Transition-metal catalyzed transfer hydrogenation using 2-propanol as a hydrogen source has become an efficient method in organic synthesis as illustrated by several useful applications reported in recent years [1a,1b]. The reaction conditions for this important process are economic, relatively mild and environmentally friendly. The most commonly used catalysts for this reaction are ruthenium(II) complexes, but some rhodium, iridium and samarium derivatives have also been used [2a–g]. In particular, half-sandwich ruthenium(II) complexes of the type [(η^6-arene)Ru(A–B)X]$^+X^-$ (where A–B is an optically pure chiral bidentate ligand and X is a halide have been found to be efficient catalyst precursors for these reactions [3]. Specifically, the (η^6-arene)Ru(TsDPEN)Cl (TsDPEN = *N*-(*p*-tolylsulponyl)-1,2-diphenylethylenediamine) system reported by Noyori et al., is among the more recently developed and efficient catalysts [4a–e]. Besides electronic effects, rigid or restrained ligands have been identified to be of pivotal importance [5a–e]. Recently, we have reported the synthesis and characterization of a variety of [(η^6-arene)Ru(P–P)Cl]PF_6 (where P–P is 2-diphenylphosphino-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene) complexes and have succeeded in the isolation of their diastereomerically pure forms [6]. However, the use of these complexes with the PF_6^- counter ion as catalysts may not be judicious, because the PF_6^- anion is prone to base promoted hydrolysis under the reaction conditions used during the catalytic process. To avoid this complication and as part of a study aimed at expanding the synthetic utility of these arene–ruthenium(II) complexes, herein, we report the synthesis of conformationally rigid [(η^6-arene)-Ru(II)(P–P)Cl]CF_3SO_3 (arene = C_6H_6 (**1**), *p*-MeC_6H_5-$CHMe_2$ (**2**), 1,3,5-$Me_3C_6H_3$ (**3**), and Me_6C_6 (**4**)) complexes (with triflate as a counter ion) and their application for the transfer hydrogenation of ketones. The highly efficient and diastereoselective [4+2] Diels–Alder *cyclo*-addition methodology was employed for

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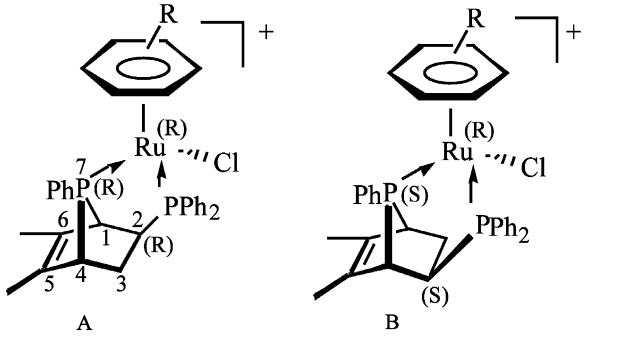
the synthesis of these complexes [7a–g]. These complexes are easily prepared and are air and moisture stable crystalline materials.

2. Results and discussion

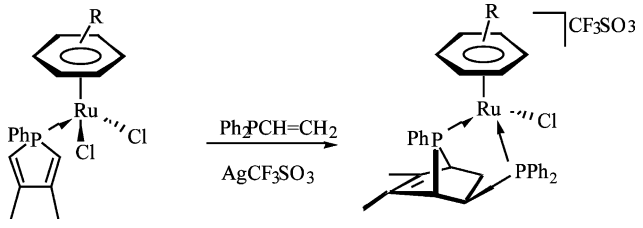
2.1. Synthesis and characterization of 1–4

The complexes were prepared by treating a dichloromethane solution of [(η^6-arene)Ru(DMPP)Cl_2] (arene = C_6H_6 (**1**), *p*-$MeC_6H_5CHMe_2$ (**2**), 1,3,5-$Me_3C_6H_3$ (**3**), and Me_6C_6 (**4**)) with one equivalent of diphenylvinylphosphine (DPVP) in the presence of $AgCF_3SO_3$ (Scheme 1).

After addition of the DPVP the reaction mixtures were stirred for 72 h at ambient temperature in the dark. Upon workup the products were isolated as orange–yellow air and moisture stable powders. Preliminary, $^{31}P\{^1H\}$-NMR analysis of the crude reaction mixture suggested the presence of two diastereomers in the ratios: **1a**:**1b** > 1:100, **2a**:**2b** 1:9, **3a**:**3b** > 1:100 and **4a**:**4b** 1:19. These two racemic diastereomers illustrated below, and for simplicity designated as A and B, respectively, may be distinguished by $^{31}P\{^1H\}$-NMR spectroscopy. In general [6] the chemical shift difference of the phosphorus resonances, $\Delta\delta = \delta P_7 - \delta P_2$ is greater for diastereomer A than for diastereomer B (vide infra). On this basis, we conclude that the major diastereomer is B in each case, the thermodynamically more stable diastereomer as was also found for the PF_6^- analogs [6].



Because the [4+2] Diels–Alder cycloadditions all occur intramolecularly [7a–f] within the ruthenium coordination sphere to form the *syn-exo*-7-phosphanorbornene skeleton (illustrated above) the absolute configuration of the C(1) and C(4) stereocenters are fixed relative to P(7) and only those at the C(2) (the ring conjunction carbon) and P(7) may vary. For these complexes the stereochemistry of C(2) is the same as that of P(7). Thus, for ease of discussion, we will refer to the absolute configuration of the chiral ligand by a single descriptor R or S. Ruthenium becomes a stereocenter in the products and may have either R or S absolute configuration leading to racemic diastereomers **A** ($R_{Ru}R_{P7}R_{C2}/S_{Ru}S_{P7}S_{C2}$) and **B** ($R_{Ru}S_{P7}S_{C2}/S_{Ru}R_{P7}R_{C2}$). Crystallization of the diastereomeric mixtures from nitromethane–ether solution afforded orange crystals which correspond to the major diastereomers as confirmed by X-ray crystallography and $^{31}P\{^1H\}$-NMR spectroscopy. The structures of **2**, **3** and **4** were determined by X-ray crystallography. In all the three structures, the geometry around the ruthenium center is pseudo-octahedral with the η^6-arene, the asymmetric bidentate phosphine and the chloride atom completing the coordination sphere. Views of the cations are given in Figs. 1–3. Crystallographic data are summarized in Table 1 and selected bond lengths and angles are presented in Table 2. Although the complexed aromatic rings in **2**, **3** and **4** are almost planar, there is a significant variation in the Ru–C (arene) bond distances. As can be seen from Table 2 the Ru(1)–C(1) (2.340(5) Å), Ru(1)–C(2) (2.296(6) Å) and Ru(1)–C(4) (2.304(5) Å) bond distances for **2** are significantly longer than the Ru(1)–C(5) (2.205(5) Å) and Ru(1)–C(6) (2.224(5) Å) bond distances. Similarly the Ru(1)–C(3) (2.299(8) Å), Ru(1)–C(4) (2.298(8) Å) and Ru(1)–C(5) (2.313(7) Å) bond distances for **3** are significantly longer than the Ru(1)–C(1) (2.236(7) Å) and Ru(1)–C(6) (2.224(7) Å) bond distances. And, for **4** the Ru(1)–C(3) (2.336(8) Å), Ru(1)–C(4) (2.321(8) Å), Ru(1)–C(5) (2.310(7) Å) and Ru(1)–C(6) (2.329(7) Å) bond



Scheme 1.

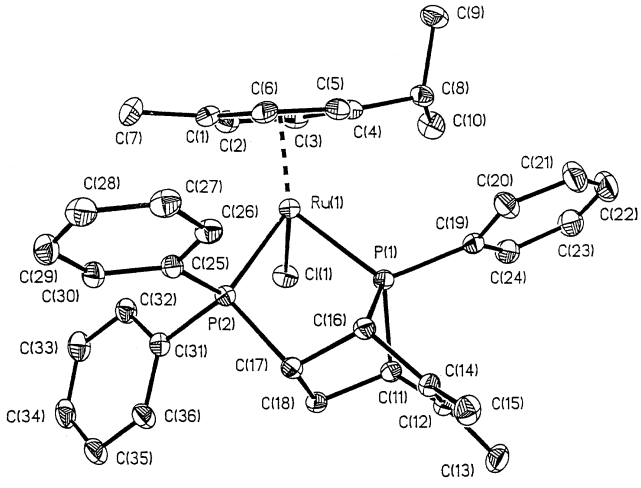


Fig. 1. Structural drawing of the cation of **2** showing the atom numbering scheme (20% probability thermal ellipsoids). Hydrogen atoms are omitted for clarity.

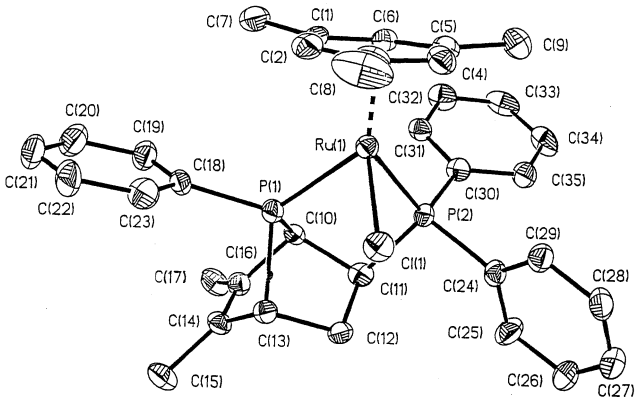


Fig. 2. Structural drawing of the cation of **3** showing the atom numbering scheme (20% probability thermal ellipsoids). Hydrogen atoms are omitted for clarity.

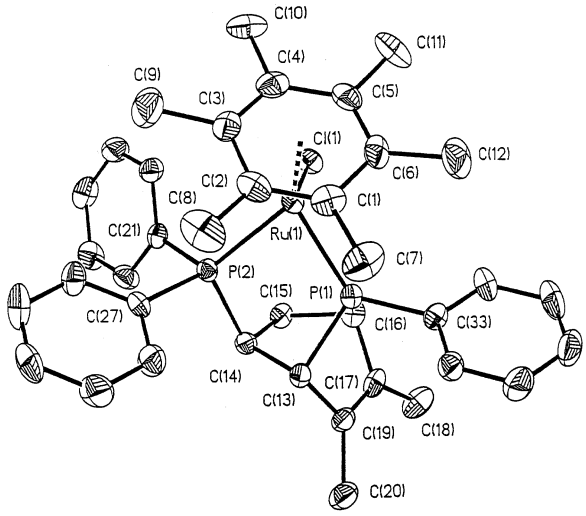
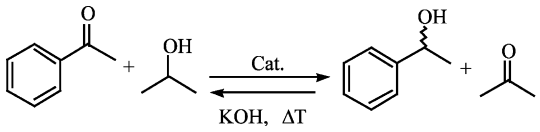


Fig. 3. Structural drawing of the cation of **4** showing the atom numbering scheme (30% probability thermal ellipsoids). Hydrogen atoms are omitted for clarity.

distances are significantly longer than the Ru(1)–C(1) (2.262(7) Å) and Ru(1)–C(2) (2.280(8) Å) bond distances. These distortions probably arise from the steric constraints imposed by the asymmetric bidentate phoshine and the *trans* influence of the phosphorus ligands [8]. These bond length data indicate that the complexes could easily slide across the face of the arene to reach the η^4-coordination mode (during the catalytic process) and hence provide access to a vacant coordination site on the metal [9a–c]. As expected, their ^{1}H-, ^{13}C{^{1}H}-, and ^{31}P{^{1}H}-NMR spectra are consistent with those reported for the analogous complexes with the PF_6^- counter ion [6].

2.2. Catalytic transfer hydrogenation of ketones

The conformationally rigid ruthenium(II) complexes **1**–**4** catalyze the reduction of ketones to the corresponding alcohols via hydrogen transfer from 2-propanol with KOH as the promoter. As the starting point, the performance of the catalysts in the transfer hydrogenation was screened by using acetophenone as a model substrate (Eq. (1)).



(1)

In a typical experiment the preformed, isolated crystalline catalyst (0.05 mmol) was dissolved by heating in 2-propanol for 15 min. After the catalysts had completely dissolved, acetophenone (10.0 mmol) and a solution of KOH (0.25 mmol) in 2-propanol were successively added and the reaction was performed at 82 °C. The reactions were conducted at a substrate/catalyst/base (S/C/base) molar ratio of 200:1:5. Under the reaction conditions complex **3** proved to be most effective catalyst relative to **1**, **2** and **4**. For instance the observed turnover frequency (TOF) measured during the first 10 min for **3** is 1004 per h whereas those of **1**, **2** and **4** are 115, 308 and 571 h^{-1}, respectively. The reduction of acetophenone with **3** was completed within 1/2 h in 98% isolated yield. In contrast, acetophenone was reduced within 3–5 h using **1**, **2**, and **4** in 95, 93 and 95% isolated yield, respectively. The progress of the transfer hydrogenation of acetophenone using **3** as a catalyst is shown in Fig. 4.

As the cationic Ru(II) complex **3** appeared to be the most active precursor for the transfer hydrogenation, the reduction of ketones other than acetophenone was attempted in the presence of **3**. A variety of ketones (S/C/base molar ratio 200:1:5) were transformed to the corresponding secondary alcohols. Typical results are shown in Table 3. The catalyst performed similarly with *m*-methoxy acetophenone. However, the reduction of *p*-methoxy acetophenone tends to proceed at significantly lower rate and yield. Complex **3** also catalyzed the transfer hydrogenation of 1- or 2-acetonaphthone very effectively but at different rates (Table 3, entries 5 and 6). Moreover, complex **3** shows good activity in the transfer hydrogenation of both five- and six-membered cyclic ketones (Table 3, entries 7 and 8). Interestingly, **3** also catalyzed the reduction of methyl isobutyl ketone (Table 3, entry 9). In most cases, the conversions to the respective alcohols were essentially quantitative and comparable to those found for acetophenone. The reaction proceeds even at a lower catalyst loading (S/C/base ratio 1000:1:5) although at a lower rate (required 4 h reaction time with **3**). The influence of different inorganic bases on the catalytic activity was also investigated. Addition of bases like KOH, NaOH or Na-(^{i}OPr) leads to similar final conversion, but the highest rate was observed when KOH was employed. In contrast to what is observed for Noyori's [4e] catalysts,

Table 1
Crystallographic data and structure refinement for **2**, **3** and **4**

Compound	**2**	**3**	**4**
Formula	$C_{38}H_{43}ClF_3O_3P_2RuS$	$C_{36}H_{38}ClF_3O_3P_2RuS$	$C_{39}H_{44}ClF_3O_3P_2RuS$
Mw	881.25	806.18	848.26
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	11.4694(14)	11.177(3)	11.233(3)
b (Å)	12.3129(18)	11.412(3)	11.3207(19)
c (Å)	15.6882(10)	14.943(3)	16.010(2)
Z	2	2	2
α (°)	96.943(9)	84.112(15)	92.906(14)
β (°)	105.962(8)	86.446(18)	93.934(14)
γ (°)	107.839(12)	72.76(2)	104.874(17)
Volume (Å^3)	1976.1(4)	1809.8(7)	1958.2(7)
ρ_{calc} (g cm^{-3})	1.481	1.479	1.439
Reflections collected	7917	7501	7913
Independent reflections	6881	6352	6804
R_1 [a]	0.0566	0.0681	0.0709
wR_2 [b]	0.1598	0.1470	0.1677
Goodness-of-fit	1.057	1.044	1.026

[a] The data were refined by the method of full-matrix least-squares on F^2, with the final R indices having $I > 2.00\sigma(I)$, $R_1 = \Sigma||F_o|-|F_c||/\Sigma F_o$.
[b] $wR_2(F^2) = \{\Sigma[w(F_o^2-F_c^2)]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table 2
Selected bond distances (Å) and bond angles (°) for **2**, **3** and **4**

	2	**3**	**4**
Bond distances			
Ru–P(1)	2.3004(4)	2.308(2)	2.293(2)
Ru–P(2)	2.3310(13)	2.324(2)	2.3395(19)
Ru–Cl	2.3925(13)	2.401(2)	2.405(2)
Ru–C(1)	2.340(5)	2.236(7)	2.262(7)
Ru–C(2)	2.296(6)	2.259(7)	2.280(8)
Ru–C(3)	2.274(5)	2.299(8)	2.336(8)
Ru–C(4)	2.304(5)	2.298(8)	2.321(8)
Ru–C(5)	2.205(5)	2.313(7)	2.310(8)
Ru–C(6)	2.224(5)	2.224(7)	2.329(7)
Bond angles			
P(1)–Ru–Cl	87.34(5)	86.99(8)	87.05(7)
P(2)–Ru–Cl	91.34(5)	91.42(7)	90.54(7)
P(1)–Ru–P(2)	79.94(5)	79.82(7)	79.29(7)

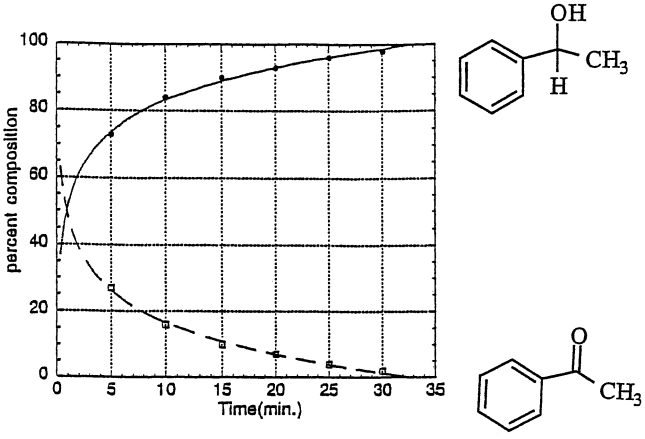


Fig. 4. Time course of the transfer hydrogenation of acetophenone using 0.5 mol% of **3** as a catalyst in 2-propanol.

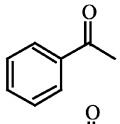
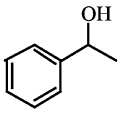
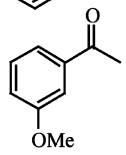
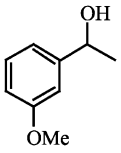
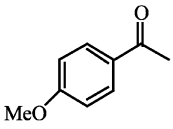
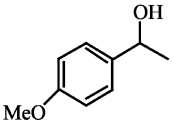
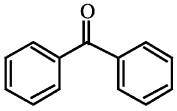
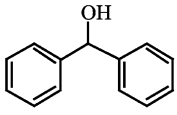
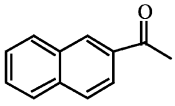
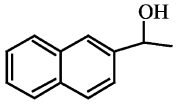
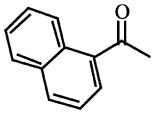
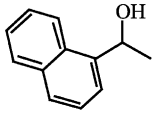
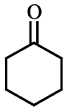
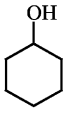
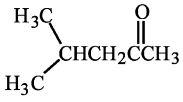
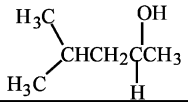
in the absence of a base no transfer hydrogenation of the ketones was observed. This suggests that a different mechanism operates than the concerted proton-transfer proposed for many Ru(aminoalcohol) systems [10]. Furthermore, the catalysts were inactive with the formic acid–triethylamine azeotrope [4d] as a hydrogen source.

The α, β-unsaturated ketone substrates are reduced both at the C=O bond and the C=C moiety; with the C=C bond being more easily reduced. Initial analysis revealed that ketones resulting from the reduction of the C=C were the major products. Other products formed are unsaturated and saturated alcohols resulting from the reduction of the C=O of the starting substrates or the subsequent reduction of the saturated ketone produced during the catalytic process (Scheme 2). The ratios of the starting ketone and the products after 48 h reaction time are (**5**:**6**:**7**:**8**) 2.7:1.8:1.7:1, respectively. These results indicate that the reduction of the activated double bond is preferred to C=O reduction which is in agreement with the general trends seen with other hydrogen transfer catalysts [11].

In contrast to what is observed for most other catalysts, a significant advantage of these catalysts is their insensitivity toward air and moisture. In this way rigorous pretreatment of solvents and substrates is avoided. Thus, reaction mixtures can be loaded into the reaction vessel in the open air and monitoring of the reaction progress also becomes very convenient. Furthermore, the ease by which these catalysts are prepared offers another important advantage.

As to the mechanism, we postulate that the active species in the reduction is a ruthenium(II) monohydride (Scheme 3). Pámies and Bäckvall [12] studied the

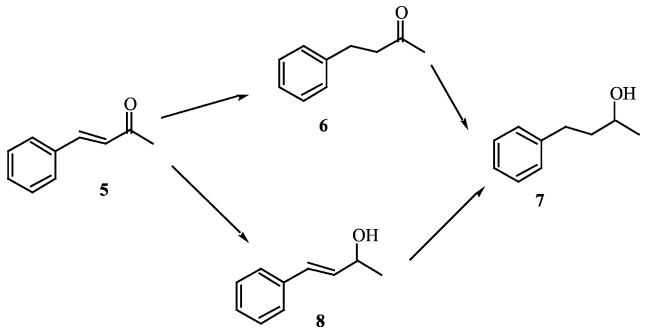
Table 3
Hydrogenation of ketones in 2-propanol catalyzed by diphosphine Ru(II) Complex[a] **3**

Entry	Substrate	Product	Time (h)	Yield(%)	TOF
1			0.5	98 (>99)[b]	1004[e]
2			0.5	96 (>99)[b]	600[e]
3			12	48[c]	188[f]
4			0.5	96 (100)[b]	600[e]
5			0.5	95 (100)[b]	629[e]
6			4	97[c]	161[f]
7			4	92[d]	155[f]
8			0.5	100[d]	622[e]
9			12	96[d]	92[f]

[a]Reaction conditions: 0.2 M substrate solution, molar ratio S/C/base 200:1:5 and 82 °C temperature.
[b]Isolated yield and the bracket product yield determined by GC.
[c]Product yield determined by ^{1}H-NMR.
[d]Product yield determined by GC.
[e]Turnover frequency: moles of product per mole of catalyst per hour, in h^{-1} measured during the first 10 and
[f]30 min, respectively.

mechanism for a number of bisphosphineruthenium(II) complexes by monitoring the racemization of monodeuterated *S*-phenylethyl alcohol with acetophenone and found that the catalysts under study in most of the cases followed the monohydride pathway.

Since our catalysts are similar to those studied by Pámies and Bäckvall we assume that they follow the monohydride pathway. More recently, Noyori et al. [13] revealed that the Ru(II) catalyzed transfer hydrogenation in 2-propanol proceeded by a hydride route involving a concerted addition of a proton and hydride via a six-membered transition state. In our system, this special case of the concerted hydride and proton transfer can be excluded, since we do not have a pendant proton carrier group (e.g. NH) in our bidentate ligand. It is conceivable that a vacant coordination site on ruthenium could also arise from dissociation of one end of the diphosphine ligand. Since this diphosphine ligand is both a very good ligand and conformationally rigid we believe that the proposed ring slippage is more likely.



Scheme 2.

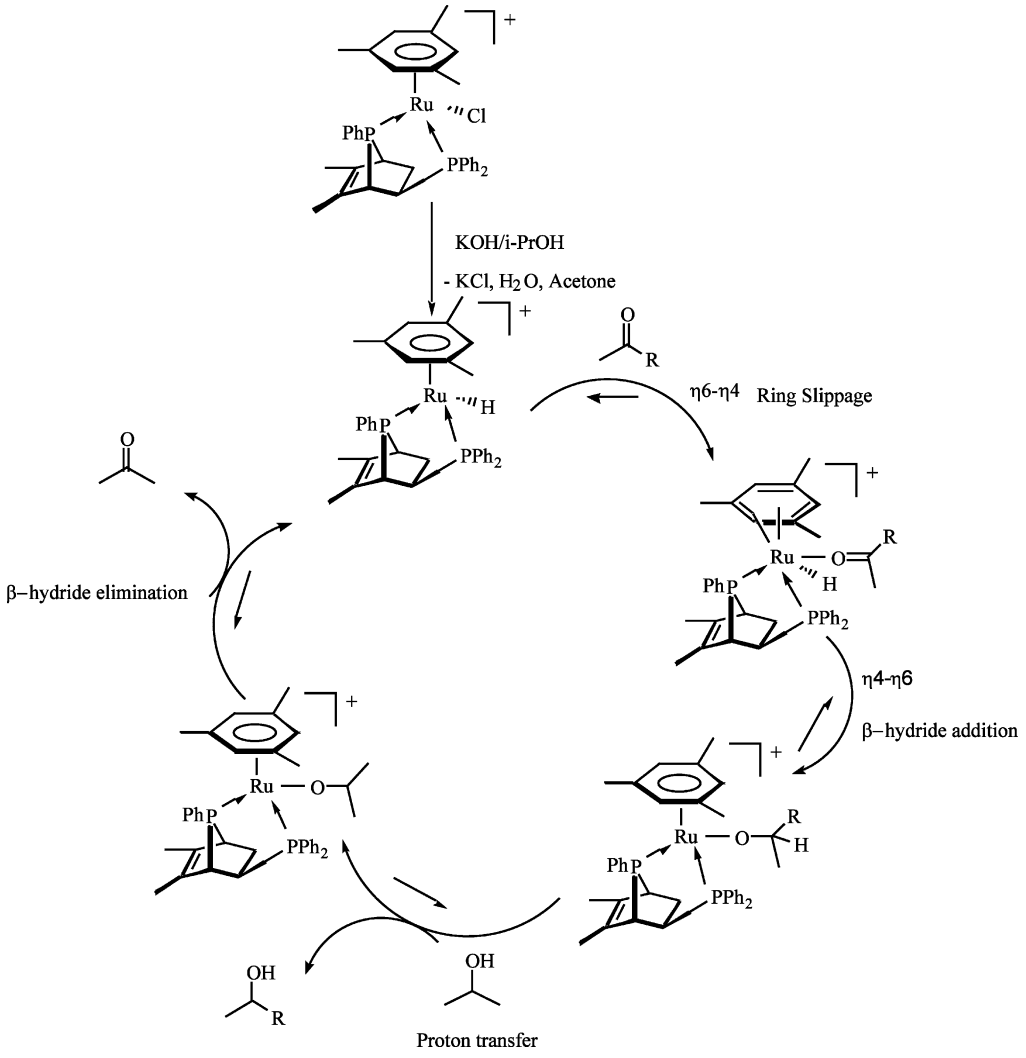
3. Concluding remarks

We have demonstrated that the racemic complex **3** is easily prepared and isolated in a diastereomerically pure form. It is an excellent catalyst for the transfer hydrogenation of a variety of ketones. We are at present preparing optically pure forms of complexes **1**–**4** so that we may probe enantiomeric excesses in these reactions.

4. Experimental

4.1. Reagents and physical measurements

All chemicals were reagent grade and were used as received or synthesized as described below. DMPP, [14] DPVP, [15] 1,3,5-trimethylcyclohexa-1,4-diene, [16] $[(\eta^6\text{-arene})RuCl_2]_2$, [17] and $[(\eta^6\text{-arene})Ru(DMPP)Cl_2]$ [18] were synthesized by literature procedures. Elemental analysis were performed by Galbraith Laboratories, Knoxville, TN. Melting points were obtained using a Mel-Temp apparatus and are uncorrected. NMR spectra were recorded on a Varian Unity Plus-500 FT-NMR spectrometer operating at 500 MHz for ^1H, 125.7 MHz for ^{13}C and 202.3 MHz for ^{31}P. Proton and carbon

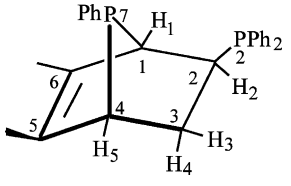


Scheme 3. Proposed schematic catalytic cycle for the transfer hydrogenation of ketones catalyzed by $[(\eta^6\text{-arene})Ru(P–P)Cl]^+$ involving a monohydride species.

chemical shifts are relative to internal Me_4Si, while phosphorus chemical shifts are relative to external 85% H_3PO_4 (aq) with positive values being downfield of the respective reference. Gas chromatographic measurements were made isothermally at 215 °C on a GOW-MAC series 150 or at 280 °C on a Hewlett-Packard HP5890 GC–MS instrument, 20% DC200 on Chromosorb P (10.16, 0.64 cm) or HP-1 (cross linked methyl siloxane) columns (2.5 m, 0.11 μm) were used.

4.2. General procedure for the synthesis of the complexes

The complexes were all synthesized by the following general procedure. To a solution containing 0.5 mmol of the [(η^6-arene)Ru(DMPP)Cl_2] complex in 40 ml CH_2Cl_2 was added 0.5 mmol of solid $AgCF_3SO_3$ in the dark. The reaction mixture was purged with nitrogen for 15 min. Then 0.6 mmol of diphenylvinylphosphine (DPVP) was added via syringe. After the addition of the DPVP the solution was stirred for 72 h under nitrogen at ambient temperature. The red color of the solution gradually became orange during the progress of the reaction. The solution was filtered through celite to remove AgCl. The volume of the filtrate was reduced to ca. 5 ml by rotary evaporation and ether was added to precipitate the products. The resulting orange–yellow precipitates were isolated by filtration, washed with ether and dried under vacuum at ambient temperature.



Compound **1**: m.p. 258–260 °C (59% yield); Anal. Calc. for $C_{33}H_{32}ClF_3O_3P_2RuS$: C, 51.87; H, 4.22. Found: C, 51.54; H, 4.38%.

^{1}H-NMR (499.827 MHz, CD_3NO_2, 25 °C).

δ 7.99 (m, 2H, H_o), 7.83 (m, 2H, H_o), 7.63 (m, 6H, H_m), 7.52 (m, 5H, $H_{o,p}$), 5.65 (s, 6H, CH, arene), 3.94 (appt td, $^3J(H_1H_2) = {}^4J(H_1H_5) = 2.0$ Hz, $^2J(PH) = 1.5$ Hz, 1H, H_1), 3.53 (appt ddtt, $^3J(PH) = 42.5$ Hz, $^2J(PH) = 10.0$ Hz, $^3J(H_2H_4) = 8.5$ Hz, $^3J(H_2H_3) = 3.0$ Hz, $^3J(H_1H_2) = 1.5$ Hz, 1H, H_2), 3.27 (appt dt, $^2J(PH) = 3.5$ Hz, $^4J(H_1H_5) = {}^3J(H_3H_5) = 1.5$ Hz, 1H, H_5), 2.39 (dddd, $^3J(PH) = 23.5$ Hz, $^2J(H_3H_4) = 13.0$ Hz, $^3J(H_2H_3) = 3.0$ Hz, $^3J(H_3H_5) = 1.5$ Hz, 1H, H_3), 1.88 (s, 3H, CH_3), 1.73 (dddd, $^3J(PH) = 24.5$ Hz, $^3J(PH) = 20.5$ Hz, $^2J(H_3H_4) = 13.0$ Hz, $^3J(H_2H_4) = 8.5$ Hz, 1H, H_4), 1.54 (s, 3H, CH_3).

^{13}C{^{1}H}-NMR (125.692 MHz, CD_3NO_2, 25 °C).

δ 138.97 (dd, $^2J(PC) = 2.8$ Hz, $^4J(PC) = 1.5$ Hz, C_5), 135.09 (d, $^1J(PC) = 46.0$ Hz, C_i), 134.78 (d, $^2J(PC) = 9.9$ Hz, C_o), 131.92 (dd, $^1J(PC) = 43.1$ Hz, $^3J(PC) = 1.4$ Hz, C_i), 131.57 (d, $^4J(PC) = 2.4$ Hz, C_p), 131.46 (d, $^4J(PC) = 2.3$ Hz, C_p), 131.34 (dd, $^2J(PC) = 17.0$ Hz, $^4J(PC) = 1.3$ Hz, C_6), 131.04 (d, $^4J(PC) = 2.8$ Hz, C_p), 130.98 (d, $^2J(PC) = 9.2$ Hz, C_o), 130.92 (bd, $^2J(PC) = 9.2$ Hz, C_o), 129. 17 (d, $^3J(PC) = 10.1$ Hz, C_m), 129.10 (bd, $^3J(PC) = 8.8$ Hz, C_m), 128.74 (d, $^3J(PC) = 10.9$ Hz, C_m), 128.25 (d, $^1J(PC) = 51.8$ Hz, C_i), 121.07 (q, $^1J(CF) = 320.9$ Hz, CF_3), 95.63 (t, $J(PC) = 2.3$ Hz, C, arene), 57.45 (dd, $^1J(PC) = 37.6$ Hz, $^2J(PC) = 12.7$ Hz, C_1), 47.66 (dd, $^1J(PC) = 33.4$ Hz, $^3J(PC) = 1.6$ Hz, C_4), 31.09 (dd, $^1J(PC) = 39.2$ Hz, $^2J(PC) = 30.8$ Hz, C_2), 30.23 (dd, $^2J(PC) = 9.2$ Hz, $^2J(PC) = 2.1$ Hz, C_3), 13.89 (appt, $^3J(PC) = {}^4J(PC) = 2.1$ Hz, CH_3), 12.35 (d, $^3J(PC) = 3.4$ Hz, CH_3).

^{31}P{^{1}H}-NMR (202.329 MHz, CD_3NO_2, 25 °C).

δ 141.99 (d, $^2J(PP) = 58.1$ Hz, 1P, P_7), 59.51 (d, $^2J(PP) = 58.1$ Hz, 1P, P_2).

Compound **2**: m.p. 201–203 °C (72% yield); Anal. Calc. for $C_{37}H_{40}ClF_3O_3P_2RuS$: C, 54.18; H, 4.92. Found: C, 53.96; H, 5.08%.

^{1}H-NMR (499.827 MHz, CD_3NO_2, 25 °C)

δ 7.93 (m, 2H, H_o), 7.79 (m, 2H, H_o), 7.66 (m, 2H, H_p), 7.56 (m, 9H, $H_{o,m,p}$), 5.91 (dd, $^3J(HH) = 6.5$ Hz, $J(PH) = 1.0$ Hz, 1H, CH, arene), 5.62 (d, ^3J)HH) = 6.5 Hz, 1H, CH, arene), 5.45 (d, $^3J(HH) = 6.5$ Hz, 1H, CH, arene), 5.22 (d, $^3J(HH) = 6.5$ Hz, CH, arene), 3.87 (app q, $^4J(H_1H_5) = {}^3J(H_1H) = {}^2J(PH) = 2.0$ Hz, 1H, H_1), 3.56 (dddd, $^3J(PH) = 41.5$ Hz,, $^3J(H_2H_4) = 9.5$ Hz, $^2J(PH) = 5.5$ Hz,, $^3J(H_1H_2) = 2.0$ Hz, $^3J(H_2H_3) = 0.5$ Hz,1H, H_2), 3.19 (dd, $^4J(H_3H_5) = 4.0$ Hz, $^4J(H_1H_5) = 2.0$ Hz, 1H, H_5), 2.40 (dddd, $^3J(PH) = 23.5$ Hz, $^2J(H_3H_4) = 13.3$ Hz, $^3J(H_3H_5) = 4.0$ Hz, $^3J(H_2H_3) = 0.5$ Hz, 1H, H_3), 2.10 (septet, $^3J(HH) = 7.0$ Hz, 1H, CH), 1.94 (s, 3H, CH_3), 1.71 9 (s, 3H, CH_3), 1.49 (s, 3H, CH_3), 1.09 (d, $^3J(HH) = 7.0$ Hz, 3H, CH_3), 0.93 (d, $^3J(HH) = 7.0$ Hz, 3H, CH_3).

^{13}C{^{1}H}-NMR (125.691 MHz, CD_3NO_2, 25 °C).

δ 139.05 (dd, $^2J(PC) = 2.6$ Hz, $^3J(PC) = 1.3$ Hz, C_6), 134.80 (d, $^1J(PC) = 44.5$ Hz, C_i), 134.53 (d, $^2J(PC) = 9.8$ Hz, C_o), 131.99 (d, $^4J(PC) = 2.6$ Hz, C_p), 131.70 (dd, $^1J(PC) = 41.2$ Hz, $^3J(PC) = 1.6$ Hz, C_i), 131.42 (d, $^4J(PC) = 2.3$ Hz, C_p), 131.36 (d, $^4J(PC) = 2.5$ Hz, C_1), 131.31 (d, $^3J(PC) = 2.3$ Hz, C_m), 131.03 (d, $^2J(PC) = 8.0$ Hz, Co), 131.00 (dd, $^2J(PC) = 15.6$ Hz, $^4J(PC) = 1.1$ Hz, C_5), 129.41 (d, $^1J(PC) = 49.5$ Hz, C_i), 129.25 (d, $^3J(PC) = 10.1$ Hz, C_m), 128.63 (d, $^3J(PC) = 10.8$ Hz, C_m), 121.06 (q, $^1J(PC) = 320.8$ Hz, CF_3), 118.63 (s, C, arene), 106.59 (d, $J(PC) = 1.3$ Hz, C, arene), 98.20 (dd, $J(PC) = 3.0$,1.6 Hz, C, arene), 95.57 (dd, $J(PC) = 2.8$,1.6 Hz, C, arene), 94.99 (dd, $J(PC) = 4.4$, 2.5 Hz, C, arene), 91.60 (d, $J(PC) = 4.9$ Hz, C,arene), 57.45 (dd, $^1J(PC) = 36.6$ Hz, $^2J(PC) = 12.6$ Hz, C_1), 48.71 (dd, $^1J(PC) = 33.4$ Hz, $^3J(PC) = 1.5$ Hz, C_4), 31.25 (dd, $^1J(PC) = 39.6$ Hz, $^2J(PC) = 30.3$ Hz, C_2), 30.43 (dd, $^2J(PC) = 10.9$ Hz, $^2J(PC) = 2.3$ Hz, C_3), 29.82 (s, CH), 21.20 (s, CH), 20.64 (s, CH_3), 17.76 (s, CH_3),13.89 (appt, $^3J(PC) = {}^4J(PC) = 1.6$ Hz, CH_3), 12.31 (d, $^3J(PC) = 3.5$ Hz, CH_3).

$^{31}P\{^{1}H\}$-NMR (202.329 MHz, CD_3NO_2, 25 °C).

Major: δ 142.07 (d, $^{2}J(PP) = 56.4$ Hz, 1P, P_7), 58.38 (d, $^{2}J(PP) = 56.4$ Hz, 1P, P_2); Minor: 140.20 (d, $^{2}J(PP) = 51.3$ Hz, 1P, P_7), 46.30 (d, $^{2}J(PP) = 51.3$ Hz, 1P, P_2).

Compound **3**: m.p. 250–252 °C (62% yield); Anal. Calc. for $C_{36}H_{38}ClF_3O_3P_2RuS$: C, 51.63; H, 4.75; Found: C, 51.45; H, 4.62%.

^{1}H-NMR (499.827 MHz, CD_3NO_2, 25 °C).

δ 7.95 (m, 2H, H_o), 7.79 (bs, 2H, H_o), 7.68 (m, 6H, $H_{m,p}$), 7.55 (m,3H, $H_{m,p}$), 7.36 (m, 2H, H_o), 5.91 (dd, $^{3}J(HH) = 6.5$ Hz, $J(PH) = 1.0$ Hz, 1H, CH, arene), 5.62 (d, ^{3}J)HH) = 6.5 Hz, 1H, CH, arene), 5.12 (s, 3H, CH, arene), 3.87 (app t, $^{3}J(H_1H_2) = {}^{4}J(H_1H_5) = 2.0$ Hz, 1H, H_1), 3.35 (dddd, $^{3}J(P_7H) = 42.5$ Hz,, $^{3}J(H_2H_4) = 9.0$ Hz, $^{2}J(PH) = 8.0$ Hz, $^{3}J(H_1H_2) = 2.0$ Hz, 1H, H_2), 3.09 (dd, $^{4}J(H_3H_5) = 3.8$ Hz, $^{4}J(H_1H_5) = 2.0$ Hz, 1H, H_5), 2.30 (ddd, $^{3}J(PH) = 24.0$ Hz, $^{2}J(H_3H_4) = 13.3$ Hz, $^{3}J(H_3H_5) = 3.8$ Hz,1H, H_3), 1.95 (s, 9H, CH_3, arene),1.91 (s, 3H, CH_3), 1.57 (dddd, $^{3}J(P_7H) = 24.5$ Hz, $^{3}J(PH) = 19.5$ Hz, $^{2}J(H_3H_4) = 13.3$ Hz, $^{3}J(H_2H_4) =$ 9.0 Hz, 1H, H_4), 1.41 (s, 3H, CH_3).

$^{13}C\{^{1}H\}$-NMR (125.691 MHz, CD_3NO_2, 25 °C).

δ 138.84 (dd, $^{2}J(PC) = 2.6$ Hz, $^{3}J(PC) = 1.0$ Hz, C_6), 135.39 (bs, C_o), 135.03 (d, $^{1}J(PC) = 43.4$ Hz, C_i), 132.03 (d, $^{2}J(PC) = 9.0$ Hz, C_o), 131.70 (d, $^{4}J(PC) = 2.5$ Hz, C_p), 131.43 (d, $^{4}J(PC) = 2.6$ Hz, C_p), 131.40 (d, $^{4}J(PC) = 2.4$ Hz, C_p), 131,39 (dd, $^{1}J(PC) = 30.7$ Hz, $^{3}J(PC) = 1.6$ Hz, C_i), 130.70 (d, $^{2}J(PC) = 15.3$ Hz, C_5), 129.10 (d, $^{3}J(PC) = 9.8$ Hz, C_m), 128.81 (d, $^{3}J(PC) =$ 10.8 Hz, C_m), 128.30 (bs, C_m), 126.88 (d, $^{1}J(PC) = 51.4$ Hz, C_i), 121.04 (q, $^{1}J(CF) = 320.9$ Hz, CF_3), 108.65 (dd, $J(PC) = 2.4$, 1.1 Hz, C_q), 97.47 (t, $J(PC) = 0.5$ Hz, CH), 55.71 (dd, $^{1}J(PC) = 35.9$ Hz, $^{2}J(PC) = 12.2$ Hz, C_1), 49.02 (dd, $^{1}J(PC) = 34.4$ Hz, $^{3}J(PC) = 1.4$ Hz, C_4), 33.42 (dd, $^{1}J(PC) = 40.3$ Hz, $^{2}J(PC) = 29.9$ Hz, C_2), 31.09 (dd, $^{2}J(PC) = 9.9$ Hz, $^{2}J(PC) = 1.9$ Hz, C_3), 17.41 (s, CH_3, arene), 13.82 (appt, $^{3}J(PC) = {}^{4}J(PC) = 1.9$ Hz, CH_3), 12.27 (d, $^{3}J(PC) = 3.5$ Hz, CH_3).

$^{31}P\{^{1}H\}$-NMR (202.329 MHz, CD_3NO_2, 25 °C).

δ 141.93 (d, $^{2}J(PP) = 58.0$ Hz, 1P, P_7), 59.68 (d, $^{2}J(PP) = 58.0$ Hz, 1P, P_2).

Compound **4**: m.p. 283–285 °C, (80% yield); Anal. Calc. for $C_{39}H_{44}ClF_3O_3P_2RuS$: C, 55.22; H, 5.22. Found: C, 55.39; H, 5.18%.

^{1}H-NMR (499.827 MHz, CD_3NO_2, 25 °C).

δ 7.83–7.35 (m, 15H, Ph), 5.91, 3.97 (app t, $^{3}J(H_1H_2) = {}^{4}J(H_1H_5) = 2.0$ Hz, 1H, H_1), 3.33 (ddddd, $^{3}J(PH) = 41.0$ Hz, $^{3}J(H_2H_4) = 9.0$ Hz, $^{2}J(PH) = 6.5$ Hz, $^{3}J(H_1H_2) = 3.0$ Hz, $^{3}J(H_1H_2) = 0.5$ Hz, 1H, H_2), 3.06 (dd, $^{4}J(H_3H_5) = 4.0$ Hz, $^{4}J(H_1H_5) = 2.0$ Hz, 1H, H_5), 2.26 (dddd, $^{3}J(PH) = 23.5$ Hz, $^{2}J(H_3H_4) = 13.5$ Hz, $^{3}J(H_3H_5) = 4.0$ Hz, 1H, H_3), 2.08 (s, 3H, CH_3), 1.71 (s, 18H, CH_3), 1.53 (dddd, $^{3}J(PH) = 23.5$ Hz, $^{3}J(PH) =$ 20.0 Hz, $^{2}J(H_3H_4) = 13.5$ Hz, $^{3}J(H_2H_4) = 9.0$ Hz, 1H, H_4), 1.36 (s, 3H, CH_3).

$^{13}C\{^{1}H\}$-NMR (125.691 MHz, CD_3NO_2, 25 °C).

δ 140.20 (s, C_o), 134.05 (d, $^{2}J(PC) = 41.6$ Hz, C_i), 132.77 (bs, C_o), 132.65 (d, $^{2}J(PC) = 12.4$ Hz, C_o), 131.52 (d, $^{4}J(PC) = 3.6$ Hz, C_p), 131.243 (d, $^{4}J(PC) = 2.6$ Hz, C_p), 131.20 (d, $^{3}J(PC) = 8.2$ Hz, C_m), 130.74 (d, $^{2}J(PC) = 15.6$ Hz, C_6), 129.62 (d, $^{2}J(PC) = 50.9$ Hz, C_i), 129.13 (d, $^{3}J(PC) = 10.9$ Hz, C_m), 129.01 (d, $^{3}J(PC) = 9.6$ Hz, C_m), 128.89 (bs, C_p), 128.60 (d, $^{4}J(PC) = 1.2$ Hz, C_p), 128.49 (d, $^{2}J(PC) = 8.0$ Hz, C_o), 123.60 (q, $^{1}J(CF) = 320.8$ Hz, CF_3), 106.32 (appt, $J(PC) = 2.0$, Hz, C arene), 58.19 (dd, $^{1}J(PC) = 33.8$ Hz, $^{2}J(PC) = 12.9$ Hz, C_1), 50.12 (dd, $^{1}J(PC) = 35.6$ Hz, $^{3}J(PC) = 1.4$ Hz, C_4), 34.26 (dd, $^{1}J(PC) = 40.0$ Hz, $^{2}J(PC) = 29.2$ Hz, C_2), 31.17 (dd, $^{2}J(PC) = 9.7$ Hz, $^{2}J(PC) = 1.1$ Hz, C_3), 14.64 (s, CH_3, arene), 13.95 (appt, $^{3}J(PC) = {}^{4}J(PC) = 1.7$ Hz, CH_3), 12.21 (d, $^{3}J(PC) = 3.3$ Hz, CH_3).

$^{31}P\{^{1}H\}$-NMR (202.329 MHz, CD_3NO_2, 25 °C).

Major: δ 148.05 (d, $^{2}J(PP) = 54.8$ Hz, 1P, P_7), 63.93 (d, $^{2}J(PP) = 54.8$ Hz, 1P, P_2); Minor: 153.29 (d, $^{2}J(PP) = 53.0$ Hz, 1P, P_7), 58.70 (d, $^{2}J(PP) = 53.0$ Hz, 1P, P_2).

4.3. Typical procedure for the transfer hydrogenation of ketones

The catalyst precursors (0.05 mmol) and 2-propanol (40 ml) were added to a three necked round bottom flask and heated under reflux for 15 min. Then the ketone (10 mmol) and KOH solution in 10 ml of 2-propanol (0.25 mmol) were introduced successively into the solution. The reaction mixture was stirred for the required reaction time. Once the reaction was complete (monitored by GC analysis) the solution was subjected to flash chromatography or filtered through silica gel. The solvent was removed by rotary evaporation to yield clear liquids or white powders. The liquids were distilled using a distillation apparatus under reduced pressure (high boiling ketones), or subjected to GC analysis (volatile ketones). The solids were analyzed by ^{1}H-NMR spectroscopy. All data are averages of two runs.

4.4. X-ray data collection and processing

Crystals of the complexes, obtained from nitromethane–ether solvent mixtures were mounted on glass fibers, coated with epoxy, and placed on a Siemens P4 diffractometer. Intensity data were taken in the ω-mode at 298 K with Mo–K_α graphite monochromated radiation ($\lambda = 0.71073$ Å). Three check reflections monitored every 100 reflections showed random ($< 2\%$) variation during the data collections. The data were corrected for Lorentz polarization effects and absorption, except for **2**, using an empirical model derived from azimuthal data collections. Scattering factors and corrections for anomalous dispersion were

taken from a standard source [19]. Calculations were performed with the Siemens SHELXTL plus version 5.10 software package on a personal computer. The structures were solved by Patterson methods. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. Hydrogen atoms were refined at calculated positions with a riding model in which the C–H vector was fixed at 0.96 Å. Compound **2** crystallized as a nitromethane solvate.

5. Supporting material

Tables of X-ray data in CIF format for compounds **2**, **3** and **4** have been deposited with the Cambridge Crystallographic Data Center, nos. CCDC 196714–196716. Copies of this information may be obtained free of charges from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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